The Cathode-Ray Fluorescence of Sodium Vapor

JAN 21 1912

BY
ROGERS HARRISON GALT

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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THE CATHODE-RAY FLUORESCENCE OF SODIUM VAPOR

By R. W. WOOD and R. H. GALT

The vapor of metallic sodium, because of its remarkable optical and spectroscopic properties, has been the subject of an extended investigation by one of the present writers, which has furnished much information regarding the mechanics of molecular radiation. When subjecting the vapor to an electric discharge, a new spectrum was accidentally discovered entirely different from anything ever seen in the flame, arc, or spark, and appearing to have no relation to the absorption, fluorescent, or magnetic rotation spectra. Cathode rays were found to excite, in addition to the green fluorescence stimulated by white light, a curious banded spectrum in the red, orange, and yellow region. A report of preliminary work on this spectrum was published in the *Philosophical Magazine* ([6] **15**, 581, 1908) and in the *Proceedings of the American Academy of Arts and Sciences* (November 1908). The present paper is a further study of this spectrum.

APPARATUS

The apparatus was essentially that described in the papers referred to. The vacuum tube was made of steel, 36 cm long and 3.3 cm in diameter, and was connected by a side tube to a mercury pump. As shown in the diagram, the steel tube itself formed the negative electrode; the positive electrode was a nickel wire carried in a glass cap cemented with sealing wax to one end of the steel tube. The electric discharge passed from the end of the nickel rod, inside the steel tube. The opposite end of the steel tube was closed by a glass or quartz window.

The current was obtained from an induction coil, built by the Roentgen Co. of Philadelphia, capable of sparking ten inches in air. The potential could be adjusted over a very wide range a (from $\frac{1}{4}$-inch spark to a 10-inch one) by almost infinitesimal steps. For

any given spark-gap, the tension on the interrupter could be so adjusted that the sparks were intermittent, perhaps one for every four or five interruptions of the current, dependent on very slight accidental variations in the resistance of the contact points.

Two spectroscopes were used. To obtain the general characteristics of the spectrum, a quartz spectrograph, made by Fuess, was employed; for accurate wave-length determinations, a Rowland concave grating of six feet radius of curvature, 15,000 lines to the inch, was used. The plates used for the red and yellow were Cramer's new "Spectrum" plates; for the green and blue, Wrattan and Wainwright's "Green Sensitive" plates.

The steel tube was heated by means of a single bunsen burner, the use of a hotter flame being prohibited by two facts: the higher the temperature, the longer was the column of vapor, and hence the greater the absorption; and, with too intense heating, it was impossible to keep the ends of the tube cool enough to prevent a fog from forming on the window. Cooling was effected by pouring cold water on cotton batting wrapped around the tube near the ends.

To obtain the spectrum, a piece of clean sodium (about 8 cubic cm) was placed in the middle of the tube, and the pressure reduced to a few millimeters of mercury. The flame was then applied and the pumping continued until most of the occluded hydrogen was removed. When the pressure was 2 mm or higher, if the current was turned on from the coil the ordinary secondary spectrum of hydrogen was obtained whether the tube was heated or cool. If the tube was kept hot at a little less than 2 mm pressure and the pressure gradually reduced, the hydrogen glow began to give way to the sodium discharge. A bright yellow ring of light, touching the inner wall of the tube, appeared over the molten sodium, and as the pressure decreased, this light became more and more intense, contracting toward the center of the tube as the cathode dark space widened. The whole of the discharge took place through the sodium vapor. The sodium light was most intense when it was scarcely possible to draw off any more gas through the pump. Then the discharge, viewed from the window at the end of the tube, appeared as an orange-yellow disk of almost insupportable brilliancy, usually completely detached from the wall of the tube.

This luminous disk evidently was the negative glow seen end-on, it being a solid cylinder along the axis of the tube, over the sodium. An image of the luminous disk was thrown on the slit of the spectroscope by means of a lens.

The nature of the discharge in the tube varies with the temperature, degree of exhaustion, and the potential applied to the electrodes. At a comparatively low temperature, when the yellow light of the sodium first appears, the negative glow had a curious appearance when viewed through the window in an oblique direction. There was an orange-yellow spot near the window, behind which the column of vapor was non-luminous; in the vicinity of the positive electrode on the other side of the dark region there was a green spot

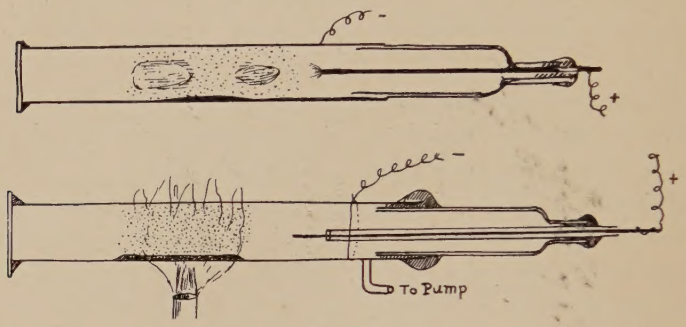
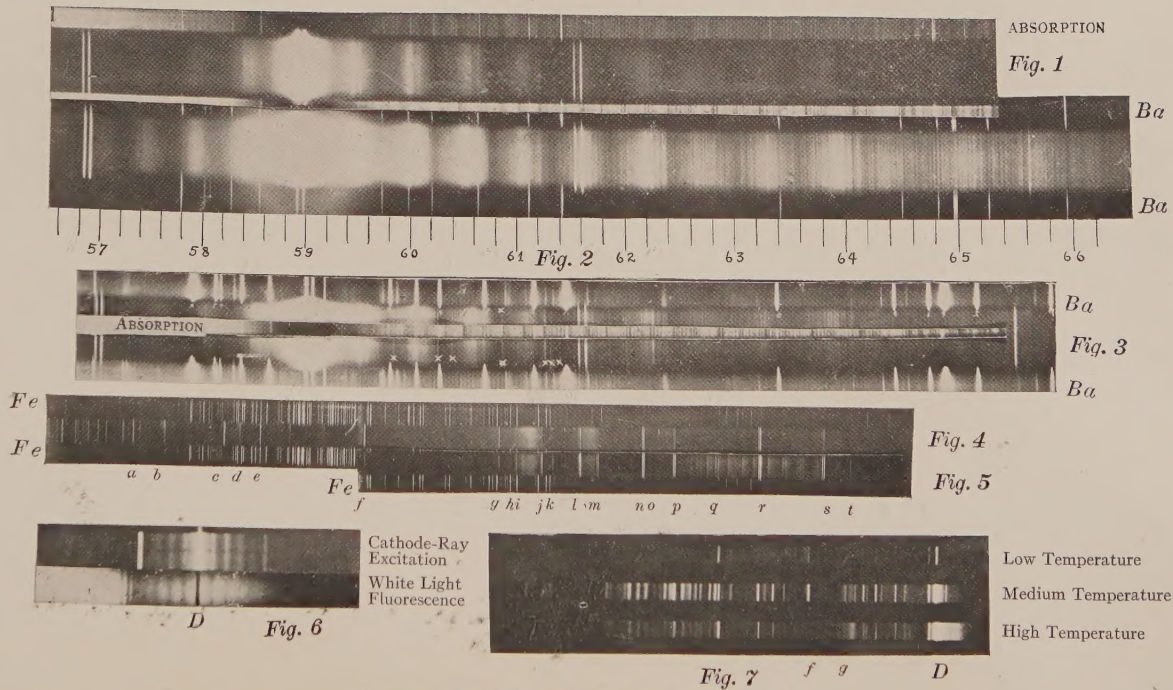


FIG. 1

of light (Fig. 1, upper figure). Viewed from the other end of the tube this spot of light was seen to be orange yellow, its apparent green color when seen through the window being evidently due to absorption. The reason why the central part of the column of vapor was non-luminous is not at once evident; but it may be that the current passed almost entirely through the vapor at the two ends of the column, where the vapor was diluted with hydrogen, the denser vapor carrying practically none of the current. This would presuppose that the sodium vapor conducts better if it is mixed with hydrogen. It is possible too that in the region where condensation is taking place the electrical properties of the vapor differ from those of the superheated vapor. Quite recently (*Physikalische Zeitschrift*, **24**, 1130, 1910) J. Koenigsberger has drawn

PLATE VI



CATHODE-RAY FLUORESCENCE OF SODIUM VAPOR

Wave-lengths corresponding to letters in Figs. 4, 5, and 7:

a, 3285	*e*, 3631	*i*, 4344	*m*, 4544	*q*, 4862
b, 3371	*f*, 3914	*j*, 4392	*n*, 4668	*r*, 4983
c, 3533	*g*, 4278	*k*, 4421	*o*, 4710	*s*, 5154
d, 3576	*h*, 4324	*l*, 4497	*p*, 4752	*t*, 5221

attention to the circumstance that with pure mercury in a very highly exhausted tube no discharge takes place even at a temperature of 150°, with a potential of 100,000 volts, either direct or alternating. It thus appears that metallic vapors do not conduct well unless mixed with small traces of some other gas.

CHARACTERISTICS OF THE SPECTRUM

1. *Red and yellow bands.*—Figs. 1 and 2 of Plate VI are from photographs made with the grating and show that the red and yellow portion of the cathode-ray fluorescent spectrum consists of a number of bands, sixteen of which are distinguishable on the negative. The negative of Fig. 1 was exposed for 30 minutes, that of Fig. 2 for three hours; with a longer exposure more bands could probably be obtained, since faint lines run out as far as λ 6864.

TABLE I

RED AND YELLOW BANDS

Band	Wave-Length	Difference	Band	Wave-Length	Difference
I.....	6565		X.....	6053	
		50 Å			53 Å
II.....	6515		XI.....	6000	
		60			54
III.....	6455		XII.....	5946	
		67			52
IV.....	6388		XIII.....	5894	
		60			51
V.....	6328		XIV.....	5843	
		52			51
VI.....	6276		XV.....	5792	
		58			48
VII.....	6218		XVI.... } *	5744	
		54	XVII... }		44
VIII.....	6164			5700	
		52			
IX.....	6112		Mean.....		54.7
		59			

* Bands not well defined.

The distance between the bands is approximately equal in a normal spectrum (see Table I), the mean difference between the centers of intensity of two adjacent bands being 54.7 $\mu\mu$. It is of course impossible to designate the exact center of any band. It is interesting to note that this spacing is of the order of magni-

tude of the spacing of the resonance fluorescent lines[1] excited in this region by the lithium lines λ 6104 and λ 6708.

These red and yellow bands are much less symmetrical than the green fluorescent bands excited by white light. The lines in these cathode-ray bands are irregularly distributed, giving no suggestion of a head or tail.

The best conditions for obtaining these red and yellow bands were: a high vacuum (about 0.1 mm); a fresh supply of sodium in the tube; high potential discharge; high temperature. The high potential was especially important. When the potential was rather low, nothing except the D lines and the lines of the subordinate series appeared; but when the e.m.f. of the coil was gradually increased, a critical value seemed suddenly to be reached at which the banded spectrum flashed out at almost full brilliancy. This e.m.f. was such as to give a spark of about seven inches in air. At high temperatures and low pressures it was sometimes found that the banded spectrum could be obtained with moderate potentials, but the brilliancy was not very great. On gradually increasing the potential, a critical point was reached at which the negative glow suddenly flashed with about tenfold intensity, becoming so bright as to be painful to the eye. If the potential was held at approximately this point, the bright discharge flashed intermittently, say once for every four or five vibrations of the interrupter, showing that the very slight accidental changes in the potential were sufficient to determine the occurrence or absence of the very brilliant discharge. It looks very much as if, for a given condition of the tube, a certain definite potential brings about a very complete ionization of the vapor, which enables it to carry a large current. If the potential drops below this value, by ever so small an amount, the ionization instantly falls to a very low value. No measurements were made of the amount of current flowing through the tube in the two conditions, a matter which should be investigated.

The red and yellow bands are made up of some 600 lines, the wave-lengths of which have been measured as a matter of record. In the present state of our knowledge regarding band spectra it

[1] R. W. Wood and F. E. Hackett, *Astrophysical Journal*, **30**, 339, 1909.

does not appear to be worth while to publish this table. Until such spectra can be decomposed into simple series, such as the resonance spectra discovered by one of the present writers, tables of the wave-lengths of the lines are of little or no value in adding to our knowledge. A comparison of these red and yellow bands with the absorption spectrum shows that there is no relation between the two spectra. Fig. 1 shows the spectra side by side, the barium arc lines being superposed upon the absorption spectrum. Fig. 1, on which the absorption spectrum was recorded with the cathode-ray spectrum, has been mounted in coincidence with Fig. 2, overlapping it a trifle in order to bring the absorption spectrum of Fig. 1 into position for comparison with Fig. 2, which shows the complete band spectrum. Short exposures were necessary to secure detail in the vicinity of the D lines, where the bands have a very great intensity. In Fig. 3 the absorption spectrum runs through the center of the cathode-ray spectrum.

A curious relation exists between the cathode-ray spectrum and the fluorescent spectrum excited by white light when the pressure of the nitrogen in the tube is about 1 cm. Fig. 6 shows that the *dark* bands of the cathode-ray spectrum coincide with the *bright* bands of the fluorescent spectrum. An entirely different fluorescence, excited by white light, in no way related to the cathode-ray spectrum, is obtained from sodium vapor when the nitrogen is at a pressure of only two or three millimeters, a matter which will require further investigation.

2. *Green bands.*—The portion of the cathode-ray spectrum lying between λ 5300 and λ 3053 is shown in Figs. 4 and 5 (Plate VI). A series of fourteen bands lies in the green, between λ 5200 and λ 4750. It is found that these coincide with the green fluorescent bands excited by white light. They appear under the same conditions as the red and yellow bands just described. Fig. 5 was made with a denser vapor than Fig. 4, and has been pasted over the iron comparison spectrum of the latter.

The coincidence of the green cathode-ray bands with the green fluorescent bands, together with the lack of agreement between the two spectra in the red, suggests that the appearance of the green bands in the cathode-ray spectrum may be a secondary effect. It

seems probable that the cathode rays excite the lines of the subordinate series (as shown in Fig. 5), which lines in turn excite by resonance the green fluorescence. The lines of the subordinate series between λ 5200 and λ 4500 are so numerous that the resonance spectrum due to them would appear almost identical with the white-light fluorescence spectrum. The absence of the resonance spectrum in the yellow and red is due to the fact that there are so few strong exciting lines in that region. This hypothesis as to the secondary origin of the green bands is supported by the fact that their intensity is much less than that of the red cathode-ray bands.

3. *Blue and violet bands.*—These bands are shown in Fig. 4; the blue band lying between λ 4541 and λ 4498, the violet band between λ 4390 and λ 4340. A weak continuation of the violet band extends as far as λ 4210. These bands are unresolved, and as we have been unable to identify them with any bands previously known, we feel disposed to refer them to sodium.

Since neither of these bands is resolved, they must be totally different from the bands found by Zickendraht[1] in this vicinity. His bands were in the spectrum of the negative pole of an arc burning in sodium vapor, at a pressure of 26 mm. He was enabled to resolve his bands with a prism giving about one-fourth the dispersion available in the present case.

Fig. 5 shows that these two bands appear under the same conditions as the red and green bands, for though the red bands do not appear in the figure, they are always very strong if there is any trace of the green bands.

4. *Ultra-violet bands.*—There are two other bands in this spectrum which lie at λ 3914 and λ 4273, each one of which consists of 10 or more well-defined lines. These are without doubt the nitrogen bands. In the plates taken with the quartz spectrograph these bands are unresolved. In some of these plates they are present with varying intensity; in other plates they are absent. There is a very strong line a little to one side of each band, which may be the head of the band. Fig. 4 shows that these bands come out strongest when the temperature is not high enough to give the other bands strongly; i.e., they are not present when the sodium vapor

[1] *Annalen der Physik*, **31**, 233, 1910.

is made dense by heating beyond a certain point. Even under these conditions they did not always appear. Their absence cannot be referred to absorption, since sodium vapor is extremely transparent in this region as has been shown by one of the present writers. The variable appearance is doubtless due to the fact that

TABLE II

λ	Intensity	λ	Intensity	λ	Intensity
5221.0	1	4308.7	1	3582	2
5153.7 } 2 S	4	4278.2	6	3576	5†
5149.2 }	3	4273.0	1	3536.5	2
4983.5 } 1 S	10	71.5	1	3533.3	10
4979.3 }	10	70	1	3371	8†
4862	1	68	1	3327.6	2
4752.2 } 2 S	5/4	65	1 *	3318.2	2
4748.3 }		62	1	3304.8 } ‡	3
4710	1	59	2	3302.8 }	3
4668.4 } 1 S	9	56	1	3285.4	8
4664.7 }	8	52	1	3274.1	3
4544.8 } 2 S	3	4248	1	3257.9	6
4541.3 }	2	4236	2	3235.0	2
4497.3 } 1 S	6	3914	10	3225.8	1
4493.8 }	5	3908.7	2	3213.6	4
4490	1	3907	3	3189.4	4
4484.5	2	3905	3	3169.2	1
4481.5	2	3903	3 *	3163.9	4
4454.5	1	3901.3	3	3158.8	2
4448	1	3898.8	3	3149.0	3
4421.9 } 2 S	2	3896.6	2	3134.9	3
4418.6 }	1	3894.0	1	3128.9	6
4404.8	1	3884.8	2	3092.3	8
4392.8 } 1 S	4	3882.6	2	3078.9 }	1
4389.4 }	3	3805.1	3	3077.4 }	3
4344.0 } 2 S	3	3754.8	2	3073.9 }	2
4341.1 }	2	3710.8	5	3055.4 }	3
4324.7 } 1 S	3	3631.6	8	3052.9 }	3
4321.4 }	2				

* Nitrogen. † Winged. ‡ Principal series.

in some cases air was admitted to the tube during the progress of the experiments.

5. *Lines.*—In addition to the bands we have numerous bright lines in the sodium spectrum. Evidently a large number of these lines belong to the first and second subordinate series.

In the ultra-violet there is a series of lines some of which coincide apparently with the spark lines while others appear to be new.

These ultra-violet lines are shown by Fig. 7 (made with quartz spectrograph) to be strongest when the bands are weak, i.e., at moderate temperatures, a circumstance resulting probably from absorption. The wave-lengths were measured on the grating photograph (Fig. 4) and are as shown in Table II, the lines of the first and second subordinate series being designated by an *S*.

At a certain stage in the warming of the sodium the band spectrum was found to contain a number of strong lines in the orange which turned out to be the secondary lines of hydrogen. When a pressure of about 1 mm was reached, just when the yellow sodium light began to appear, these hydrogen lines came out strongly. Usually they disappeared as soon as a slightly higher vacuum was obtained; but once they were present for a considerable length of time and were recorded on a plate together with the sodium spectrum. This hydrogen spectrum could be obtained with the tube cold as in an ordinary hydrogen vacuum tube. In Fig. 3 these hydrogen lines appear (each marked with an *X*) superposed on the cathode-ray spectrum.

SUMMARY

A new spectrum is obtained from the negative glow of a vacuum tube containing sodium vapor. This spectrum shows the D lines, the first and second subordinate series, the green fluorescent bands excited by white light, a series of symmetrical bands in the red and yellow, two unresolved bands in the blue and violet, and a large number of new lines, some of which may however coincide with the spark lines. The red and yellow bands and the violet bands have been found in no other spectrum of sodium vapor.

Johns Hopkins University
December 1910

BIOGRAPHY

Rogers Harrison Galt, the son of Commodore Rogers H. Galt, U.S.N., and Mary Meares, his wife, was born on July 3, 1889, in San Francisco, California. In 1904 he graduated from the public high school of Lynchburg, Va. In 1907 he received the degree of Bachelor of Arts at the Johns Hopkins University, where he began graduate work in physics in October of that year. He held a Virginia scholarship in 1907–8, and in 1909–10. He was student assistant in the Physical Laboratory in 1908–9.

During his graduate work courses have been taken under Professors Ames, Wood, Whitehead, Cohen, and Jones, Dr. Anderson, and Mr. Jewell.